

California Regional PM₁₀ and PM_{2.5} Air Quality Study (CRPAQS)

Statement of Work – CRPAQS Data Analysis Task 4.2 EMISSION INVENTORY RECONCILIATION

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Sonoma Technology, Inc.**

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Introduction

Comparisons of ambient- and emission inventory-derived primary pollutant ratios have proven to be a useful tool in improving emission inventories. However, these types of comparisons are confounded by the fact that ambient concentrations are influenced not only by fresh pollutants emitted in the near vicinity of a monitor, but also by the carryover of aged pollutants transported from sources farther away and the chemical reactions that may have occurred after the pollutants were emitted. The influence of these effects on comparisons can be minimized (but not eliminated) by selecting ambient data collected at times when emission rates are high and chemical reaction rates are low. Morning sampling periods offer the best potential to minimize the effects of the latter influences in the ambient/emission inventory comparisons. Emissions are generally high during morning hours, mixing depths are low, and long-range transport and chemical reactions are minimized. It should be recognized, however, that NO_x emissions from certain sources may be injected above the morning inversions and, hence, not affect surface-level concentrations. Evaluations with and without elevated NO_x sources will be performed in order to understand their potential influence on the results.

Atmospheric dispersion models are commonly used to understand relationships between primary emissions and ambient levels of secondary inorganic and organic aerosol species. For inorganic secondary aerosols, such as sulfate, nitrate, and ammonium, there is some history of model evaluations and refinements that is helping to build confidence in these tools. Analyses of inorganic secondary components have shown that they commonly have broad regional patterns that do not show significant correlation with local emission source strengths. For secondary organic aerosol, highly parameterized models are under development to approximate environmental chamber data and investigate all of the different volatile organic compounds (VOCs) that produce condensable products. Given uncertainties in the models and model inputs, especially regarding the yields and phase partitioning of secondary organic aerosols, we believe it will be useful to compare emissions to secondary species relationships as part of the initial data analysis. Like model development, this data analysis task is complicated by (1) the absence of methods to uniquely identify and measure all (individually or lumped) of the secondary organic aerosol species in the atmosphere and (2) the fact that secondary organic aerosols are derived from both anthropogenic and biogenic VOC emissions; in addition, biogenic VOC emissions are quite uncertain.

Scope of Work

Using ambient measurements collected during the CRPAQS field study, STI will compare emissions estimates with ambient air quality data on a seasonal and spatial basis by comparing emission inventory- and ambient-derived primary pollutant ratios of hydrocarbon/NO_x, CO/NO_x, SO₂/NO_x, PM₁₀/NO_x, PM_{2.5}/NO_x, and NH₃/NO_x. Primary pollutant ratios will be compared for three urban and two rural sites to be determined in consultation with the California Air Resources Board (ARB). The secondary inorganic aerosol components and estimates of the secondary organic aerosol components will be correlated with precursor emission source strengths at different locations for periods with similar meteorological conditions.

The scope of work for the emission inventory evaluation task will be divided into three work elements:

- Site selection and data processing
- Comparison of emission inventory and ambient primary pollutant ratios
- Evaluation of secondary organic and inorganic components

The technical approach for each of these work elements is presented below.

Site selection and data processing

STI will work with ARB to select ambient monitoring sites for which to compute pollutant ratios for comparison with the emission inventory. We will determine data requirements and summarize data availability by site for computing primary pollutant ratios and for analyzing secondary pollutants. We will produce a list of sites that have adequate air quality and meteorological data to carry out analyses. STI will work with ARB to select three urban and two rural sites suitable for performing the emission inventory evaluation, to the extent possible, on a seasonal basis.

ARB will supply STI with the latest available gridded, hourly, and speciated emission inventory being developed for PM modeling. The inventory provided by ARB will include seasonal emissions estimates for hydrocarbons, CO, NO_x, SO_x, PM_{2.5}, PM_{2.5-10}, NH₃, gaseous organic aerosol precursors, and primary aerosols and should encompass the regions surrounding the ambient monitoring sites selected for this analysis. The hydrocarbon data should be speciated into individual chemical species. The primary aerosols should be speciated into six groups: elemental carbon (EC), organic carbon (OC), sulfate (SO₄⁻), non-sea salt sodium (Na⁺), non-sea salt chloride (Cl), and other PM (which includes crustal material); the groups should then be subdivided in eight sizes. Of great importance to this effort is the ability to accurately match emissions information with ambient air quality data. The most appropriate comparisons for this type of evaluation should be based on individual chemical species, or compound groups, to the extent possible.

As part of this work element, STI will process the ambient air quality and meteorological data collected at (or near, for meteorological data) the five selected sites into formats needed for comparisons with the emission inventory. We have assumed that the data will have been

validated to Level I at the time of acquisition. We will perform statistical analyses of the ambient air quality data including calculations of minima, maxima, averages, and medians. Summary tables and charts of ambient air quality data will be prepared. In addition, validated surface meteorological data will be analyzed and average seasonal wind rose plots will be generated to understand the potential influence of the meteorology (e.g., mixing depth, plot wind speed, and direction) on the ratio comparisons. The results of these analyses will suggest whether the data collected are appropriate for this type of evaluation.

The emission inventory data obtained from ARB will be processed and analyzed. The individual chemical species reported in the inventory will be matched to those measured in the ambient data. The compounds that are not capable of being detected by the sampling and analysis methods will be ignored, and the emissions data will be converted from mass to molar units. The processed emissions data will be analyzed and summary tables will be prepared. These tables and graphs will contain emission characteristics by grid region and major source categories.

Comparison of ambient- and emission inventory-derived hydrocarbon/NO_x, CO/NO_x, SO₂/NO_x, PM/NO_x, and NH₃/NO_x

The second work element will involve computing hydrocarbon/NO_x, PM₁₀/NO_x, PM_{2.5}/NO_x, CO/NO_x, SO₂/NO_x, and NH₃/NO_x from ambient and emission inventory data. Ambient- and emission inventory-derived ratios will be compared for a selected subset of days/hours for which the ambient data meet specified selection criteria. Comparisons will be made for different spatial configurations of grid cells to determine potential meteorological effects on the ratios. Ambient-derived ratios will be compared with emission inventory-derived ratios for emissions from the grid cell where the monitor is located, as well as regions (wind quadrants) surrounding the grid cell where the monitor is located. In addition, we will evaluate the effect of elevated point sources by comparing ambient-derived ratios with emission inventory-derived ratios both including and excluding emissions from elevated point sources.

To investigate how ambient and emission inventory data vary by season and by spatial location, pollutant ratios will be computed on a seasonal basis (assuming adequate data is available by season) for up to three urban sites and two rural sites. In urban areas, emission rates are typically high during morning hours. However, this is not always the case for rural regions where high emissions rates tend to be associated with specific events or with increased seasonal emissions activities (e.g., agricultural activities and burning). Because the temporal variation in emissions activity is somewhat unpredictable for rural regions, an alternative approach will be used to compare emission inventory- and ambient-derived primary pollutant ratios.

Ambient data and known emissions activities will be examined at two rural sites. These data will be used to identify periods of high and low emissions activity, and ambient pollutant ratios will be computed for corresponding time periods resulting in a range of maximum and minimum ambient ratios to compare to the average seasonal emission inventory-derived ratio. Emission inventory- and ambient-derived ratios for hydrocarbon/NO_x, CO/NO_x, SO₂/NO_x, PM₁₀/NO_x, PM_{2.5}/NO_x and NH₃/NO_x ratios will be compared once the chemical species in the emission inventory data and the ambient data have been matched and converted to the same units. The results of the ratio analyses will be compared to findings from the carbon mass

balance (CMB) work carried out in Task 4.1 to examine emissions source contributions in the inventory and in the ambient data. The data from the ratio comparisons and emission inventory-to-CMB comparisons will be summarized in both tabular and graphical formats.

Evaluation of secondary inorganic and organic compounds

EC and primary OC are often co-emitted, and EC may, therefore, be used as a tracer of primary OC. The underlying hypothesis is that EC and primary OC often have the same sources, and, therefore, there is a representative ratio of primary OC/EC for the primary aerosol in a given area. If the measured ambient OC/EC ratio exceeds the expected ratio, the excess OC is considered to be secondary. To evaluate secondary inorganic and organic compounds, we will estimate the amount of secondary organic aerosol from the OC measurements using the OC/EC ratio approach.

The difficulty in applying this method comes in trying to establish the primary OC/EC ratio for each area. We have performed exploratory analyses using measured OC and EC data on days with conditions unfavorable for secondary organic aerosol formation, such as low sunlight or fog, low temperatures, and rapid dispersion and transport. The problem with this approach is that, given the long lifetime of OC and EC particles, it is difficult to objectively identify days with low secondary organic aerosol potential. We have also explored using all the observed OC and EC data in a region below a plausible upper limit for the primary OC/EC ratio (e.g., 2.5 – 2.9). The latter is much easier to implement and produced more consistent results in our analysis of IMS-95 data. Nevertheless, we will explore both methods and select one appropriate to use with these data. This will be done with all the filter-based OC and EC data.

In the second part of the exploratory analysis, we will compare spatial patterns of PM_{2.5} sulfate, nitrate, ammonium, and secondary organic aerosol ambient concentrations with the spatial patterns of SO₂, NO_x, NH₃, and VOC in the emission inventory. The comparisons will be made for several different seasons and meteorological conditions. We will examine emissions-air quality correlations that may be evident in this new and extensive CRPAQS data set that were not apparent in earlier, more sparse data sets.

Schedule of Deliverables

Table 1 lists the deliverables to be prepared for Task 4.2 and their planned delivery dates.

Table 1. Schedule of deliverables.

Deliverable	Deliverable Due Date
Submit final work plan	January 2002
Obtain and process air quality, meteorological, and emissions data	March 2003
Perform emissions inventory evaluation	May 2003
Perform secondary aerosol analyses	July 2003
Prepare draft technical memorandum	August 2003
Submit final technical memorandum	September 2003
Submit peer-reviewed paper and conference presentation	October 2003

Description of Deliverables

The deliverables of Task 4.2 include

- A summary of findings in the form of a draft technical memorandum
- A final technical memorandum incorporating reviewers' comments
- A paper to be submitted for publication based on the technical memorandum

The schedule for this task is somewhat dependent on the availability of results from other tasks. We have estimated a schedule as shown in Table 1. Additional time (and, potentially, resources) may be required if the products of other tasks are not received as estimated in the table.

ARB Staff Assigned to this Task

The ARB Project Manager assigned to this Task is:

Ms. Patricia Velasco

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STI Staff Assigned to this Task

Ms. Tami Funk will be the task manager for Task 4.2, and she will be assisted by Mr. Lyle Chinkin. Ms. Funk has conducted emissions inventory evaluations for several regions of the United States including emissions evaluation work in the San Joaquin Valley as part of IMS-95. In an effort to minimize duplication of data processing and analyses among tasks, Ms. Funk will work closely with Mr. Frederick Lurmann, Ms. Hilary Main, and Mr. Clinton MacDonald to coordinate and acquire air quality and meteorological data processed for other data analysis tasks.

Data Products To Be Performed/Delivered by ARB

ARB will supply STI with the latest available gridded, hourly, and speciated emission inventory developed for PM modeling. The inventory provided by ARB will include seasonal emissions estimates for hydrocarbons, CO, NO_x, SO_x, PM_{2.5}, PM_{2.5-10}, NH₃, gaseous organic aerosol precursors, and primary aerosols and should encompass the regions surrounding the ambient monitoring sites selected for this analysis. ARB will provide hydrocarbon emissions estimates speciated into individual chemical compounds. The primary aerosols should be speciated into six groups: elemental carbon (EC), organic carbon (OC), sulfate (SO₄²⁻), non-sea

salt sodium (Na^+), non-sea salt chloride (Cl^-), and other PM (which includes crustal material); the groups should then be subdivided in eight sizes. STI will work with ARB to determine how the data will be transferred to STI and in what format(s) the data will be provided.

Software and Models to be used by STI

STI will use the following software to complete work under this task:

- Microsoft Word
- Microsoft Excel
- Microsoft Access
- ArcGIS 8.2